4. Green Solvent-Based Gel Type Adsorbent Materials for Wastewater Treatment

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Abstract:

A novel type of materials for the treatment of wastewater is gel-based adsorbents with green solvents. To create them, natural or synthetic polymers are dissolved in environmentally friendly solvents such water, ethanol, glycerol, or ionic liquids, and then they are cross-linked to create a three-dimensional network. Due to their high porosity, swelling ability, and mechanical strength, the resultant gels may effectively trap a variety of wastewater contaminants, including microplastics, heavy metals, dyes, and organic compounds. Adsorbents of the green solvent-based gel type have a number of benefits over those of the traditional kind, including affordability, simplicity of synthesis, biodegradability, and recyclability. Additionally, they can be modified with functional groups or nanoparticles to improve the efficiency and selectivity of their adsorption. Green solvent-based gel type adsorbents are promising materials for the development of sustainable and efficient wastewater treatment technologies.

Keywords:

Wastewater treatment, Ionic liquids, DESs, Hydrogels, Organogels, Adsorption.

4.1 Introduction:

One of the biggest issues facing contemporary society is water contamination. Large quantities of pollutants, including heavy metals, oils, aromatic compounds, and dyes, are released as a result of industrial activity. The main effect is a decline in the supply of potable water, which is already scarce.[1]

A variety of industrial fields use dyes, including textiles, printing, plastics, food, cosmetics, paper, and others. This explains why more than 700 000 tons of dyes are produced annually. Despite rigorous environmental rules regarding their discharge and advancements in dyeing techniques, more than 15% of total production is regrettably released into the environment each year. The majority of colors are not biodegradable and thermally stable and some of their metabolites are also carcinogenic. They have the potential to influence photosynthetic activity from an environmental perspective.[1]

Adsorption is one of the most popular physical techniques. Various adsorbents, including polymers, metal-organic frameworks, carbon-based materials, natural fibers, and inorganic compounds like halloysite nanotubes, have been proposed. However, in recent years, gel phases, particularly supramolecular gels, have also been suggested as workable substitutes.

Low molecular weight gelators (LMWGs) interact weakly and cooperatively to generate these gels, which causes a fibrillary network to self-assemble and become capable of encasing solvent molecules.[1]

A hydrogel is a biphasic material that is composed of porous, permeable solids and at least 10% by weight or volume of interstitial fluid composed completely or mainly by water. Hydrogels are used in various industries due to their versatile and environmentally sensitive nature. They can come in two forms: solid and liquid. Hydrogels have many applications in the biomedical area such as wound care.[2]

Hydrogels have many benefits for green chemistry. They can dispense needed nutrients or chemicals. Hydrogels are also environmentally sensitive and versatile. They can be used in various industries such as biomedical, industrial, agricultural, electrical, healthcare, and hygienic products.[2]

Eutectogels are gels that are formed by gelling natural deep eutectic solvents (NADESs) . They are more stable than hydrogels and greener than ion gels. Eutectogels have many applications such as in the fields of food, medicine and materials.[3]

4.2 Self-Sustaining Supramolecular Ionic Liquid Gels for Dye Adsorption:

This is a new type of gel that can be used to remove dyes from water. The gel is made up of two types of molecules: an ionic liquid and a gelator. The ionic liquid is a salt that is liquid at room temperature and the gelator is a molecule that can form a gel when mixed with the ionic liquid.[1]

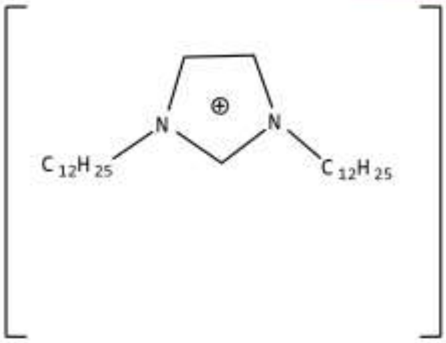
The resulting gel is self-sustaining and can be used to remove dyes from water without the need for external energy sources. The gel is self-sustaining and can be used multiple times without losing its effectiveness.[1]

Ionic liquid gels have many potential applications in a more sustainable future. They provide the ability to build functionality at every level, the solid component, the ionic liquid, and any incorporated active functional agents. Some of the potential applications include electrochemical devices, sensors, and catalysts.[1]

Some of the Rheological and Morphological studies can be carried out like Gelation Tests, Thermal Stability and Gel phases. Gelation tests were carried out both in conventional solvents and in ILs.

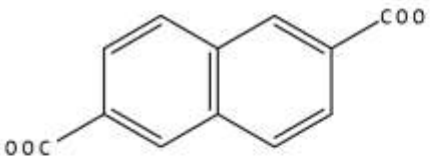
In general, salts used were soluble in alcohols and glycerol, but insoluble in highly polar solvents like water, phosphate buffer, ethylene and triethylene glycols. However, in most cases, they were completely soluble in DMSO and DMF.[1]

Gelators

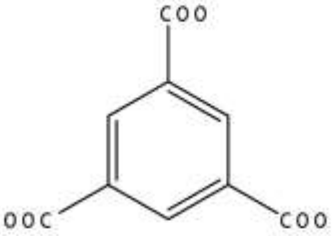


$[C_{12}C_{12}im]n[Y]$

[1,4-BDC]



[2,6-NDC]



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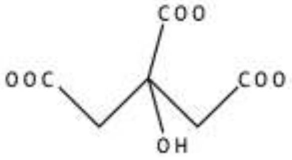

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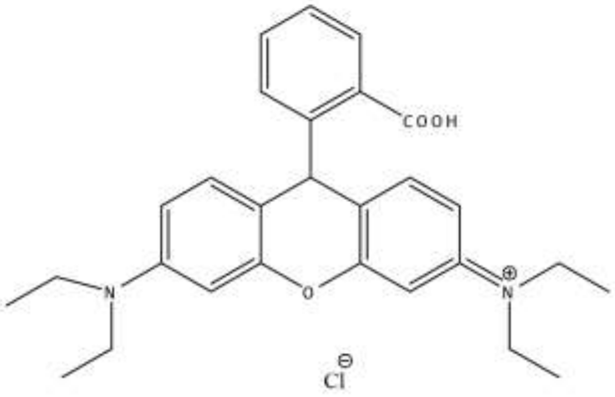
Dye



RhB

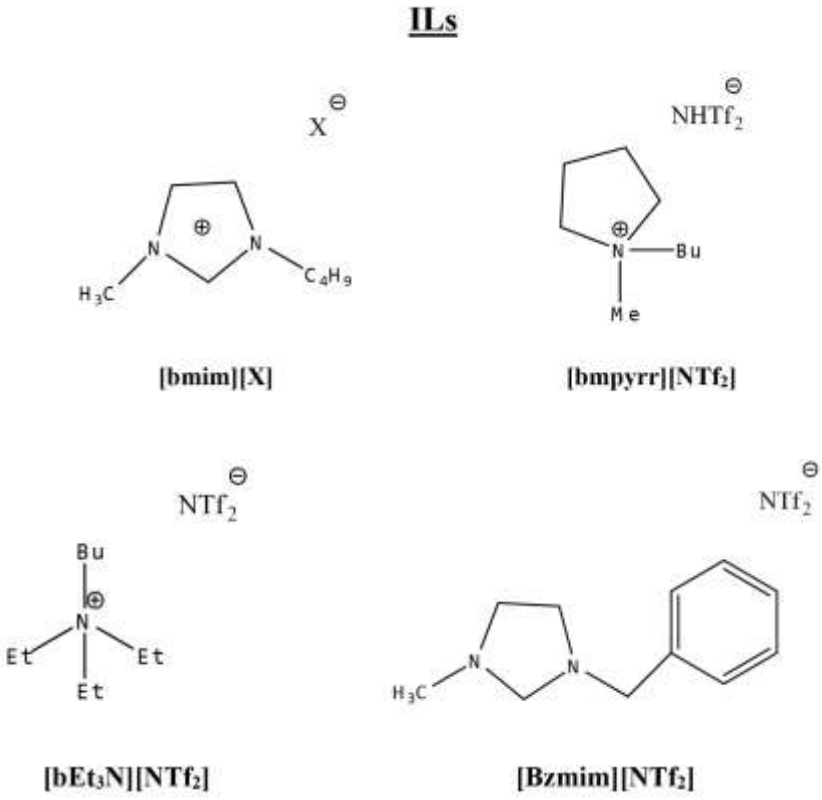


Figure 4.1: Structures of Gelators, ILs and Dye Used; Schematic Representation of the Adsorption Process.[1]

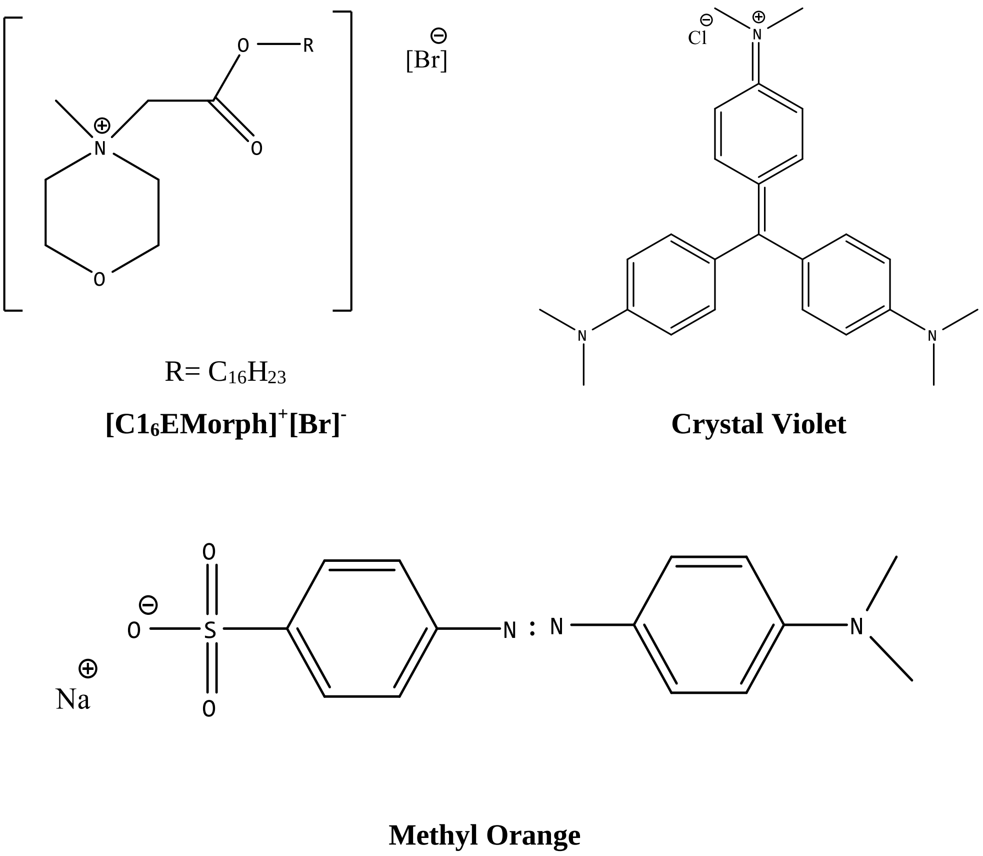
Gelling ability was tested both in conventional solvents and in ILs. Solvents having different polarities and hydrogen bond donor abilities were chosen. However, we used both aliphatic and aromatic ILs and, in the case of imidazolium-based ones, the effect due to a different sizes, shapes, and coordination abilities of the anion ([BF4]−, [PF6]−, [SbF6]−, [NTf2]−) was Analyzed.(Fig-1) Then, we tested the removal efficiency of gel phases toward a cationic dye like Rhodamine B (RhB) in a static system or in a dialysis membrane or immobilized in a column as adsorbent. In the latter case, a removal efficiency of over 95% was obtained in less than 10 min. To better modulate application of our gel phases, we first performed a complete investigation of their properties (gel−sol transition temperature, kinetic of gel phase formation, morphology, self-repairing ability, rheological behavior). The soft materials showed very interesting properties, like self-strengthening ability and good load-bearing capacity.[1]

4.3 Stimuli Responsive, Self-Sustainable, and Self-Healable Functionalized Hydrogel with Dual Gelation, Load-Bearing, and Dye-Absorbing Properties:

It describes a hydrogel that has the ability to respond to stimuli such as temperature and pH. The hydrogel is self-sustainable and self-healable. It has dual gelation properties which means it can transform from a fibrillar opaque hydrogel to a transparent hydrogel upon heating.[2]

Hydrogels comprises the most important and transformable functional class of materials due to their moderate mobility, flexibility, and physicochemical properties that could be finetuned selectively through changing the molecular structure of the gelator and/or through various external stimuli. They are formed through self-assembling low-molecular-weight gelators (LMWGs) in aqueous medium by maintaining a delicate balance between polar and nonpolar parts of the gelator. The polar part interacts favorably with water molecules and enhances its solubility, whereas the nonpolar part tends to come closer to each other and minimize their exposure toward water (hydrophobic interaction), thus facilitating self-assembly within these molecules.[4], [5]

Chemical structures



R= $C_{16}H_{23}$

[C1$_6$EMorph]$^+$[Br]$^-$

Crystal Violet

Methyl Orange

Figure 4.2: Chemical Structures of C16EMorphBr, Crystal Violet (CV) Dye and Methyl Orange (MO) Dye [2]

Here we discussed the morpholinium-based ester functionalized surfactant 4-(2-(hexadecyloxy)-2-oxoethyl)-4-methylmorpholin-4-ium bromide (C16EMorphBr) with a melting point of 78.53 °C. The surfactant has the characteristic feature of ILs (arbitrarily, ILs are defined as electrolytes with mp ≤ 100 °C) and has established surface-active properties. C16EMorphBr forms hydrogels at 7.20% (w/v) critical gel concentration and pH 7.4. The structure of the surfactant is given in (**Figure 4.2**).[2]

The formed hydrogel exhibits phase transition from opaque to transparent through changing the temperature from 25 to 50 °C. The dual gelation properties are due to the changes within its supramolecular framework from bilayer lamellar to cylindrical due to the exclusion of water molecules. This phase behavior was characterized using various state-of-the-art physical, spectroscopic, microscopy, and scattering techniques. The porous xerogel that forms after exclusion of the water molecules from the opaque gel shows self-sustaining, self-healing, moldable, and load-bearing properties. Rheology and tensile strength and compression tests were performed to study the mechanical properties of the xerogel. The same xerogel is then used as an absorbent for the selective removal of anionic dyes from an aqueous solution.[2]

Some properties and characteristics are discussed in this chapter as follows:

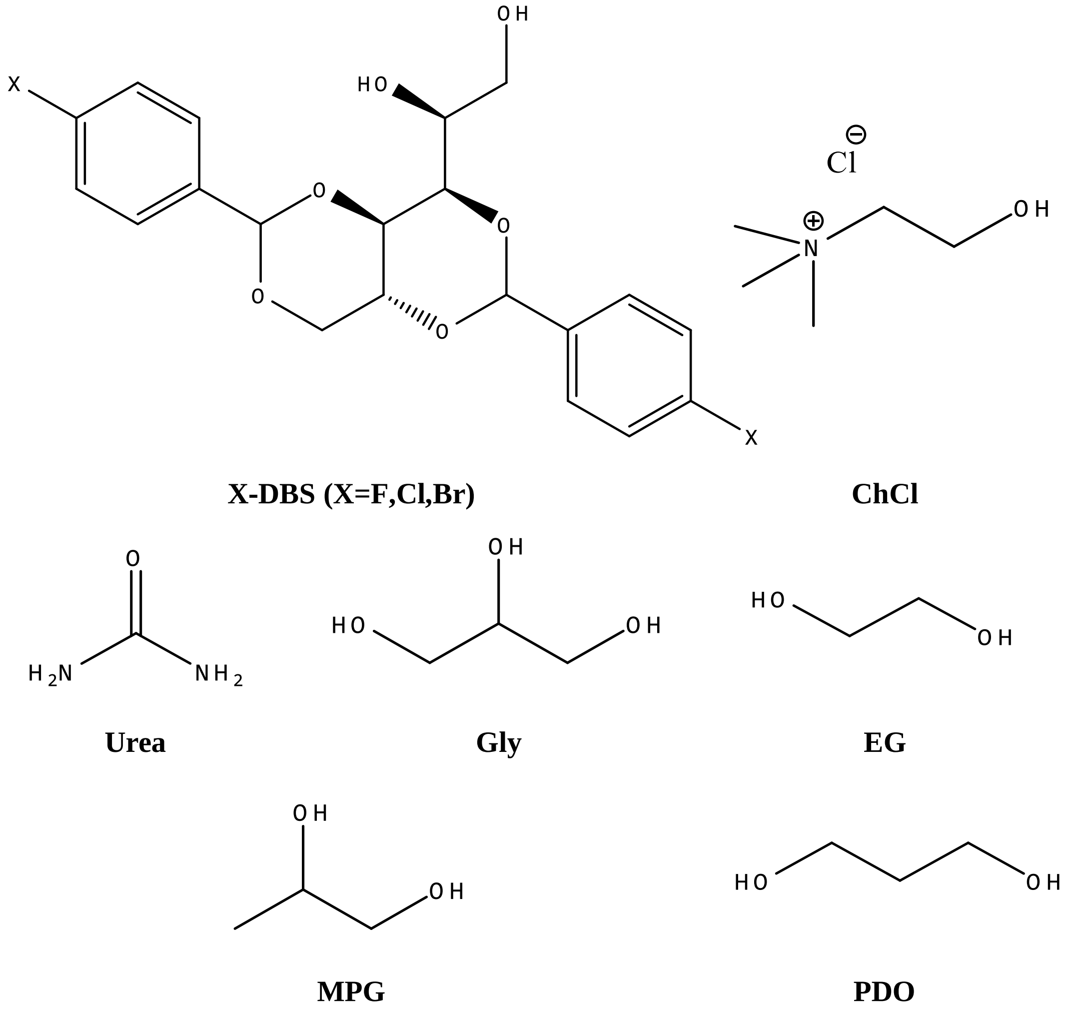
- *Gelation:* The pre-weighed solid C16EMorphBr was added in a glass vial, and 10 mL of water was added in the vial. The mixture was then heated at 60 °C on a water bath to get the transparent homogeneous solution, which was then cooled to room temperature to get the fibrillar opaque hydrogel visually (**Fig. 4**).[2]
- *Turbidity:* As a function of temperature and DSC analysis were performed to confirm the reversible transition of an opaque hydrogel into a transparent hydrogel on changing the temperature from 25 to 50 °C. The phase behavior was monitored by measuring the transmittance as a function of temperature where a dramatic increase in transmittance was observed as the temperature reached between 45.50 and 50.0 °C with visual appearance of the hydrogel turning from opaque to transparent. Explore the morphology of the hydrogel to understand the structural arrangement of the gelator within them. To do that, we have examined the morphology of the opaque gel through scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM).
- *Self-Sustaining, Self-Healing, and Load-Bearing Properties of Xerogel:* The self-sustaining nature of the xerogel indicates that the gel with immobilized solvent molecules is stable and intact and stands by itself without any support and without changing its shape such as a cylinder, ring, and rectangle. The xerogel was obtained from the removal of water from the fibrillar opaque gel. We observed that the xerogel exhibited excellent self-sustainability.
- *Thermogravimetric Analysis:* A thermogravimetric analyzer SDT Q600 was used to study the thermal stability of the gelator. The temperature range studied was between 25 and 500 °C in a N2 atmosphere at a heating rate of 10 °C/min. Tstart, the temperature at which the decomposition starts, was measured to be 198 °C for the gelator.
- *UV−Visible Spectroscopy:* The gel-to-gel transition through turbidity measurement was studied through measuring the transmittance of the hydrogel as a function of temperature from 25 to 70 °C on a Varian Cary 50 UV spectrophotometer. Dye absorption experiments were carried out at 25 °C at 463 nm (λmax of MO) and 588 nm (λmax of CV).
- *Differential Scanning Calorimetry (DSC):* The phase transition between the opaque and transparent gel and melting point of the gelator was measured by performing DSC measurements on a METTLER TOLEDO DSC 1 STARe instrument in triplicate under a
- N2 atmosphere in the temperature range of 30−90 °C at a heating rate of 2 °C min^{-1}.

- *Scanning Electron Microscopy (SEM):* A gold-coated gel was dried at 25 °C and was analyzed for its morphology by a scanning electron microscopy instrument (Hitachi S-3400 N) operated at 15 kV.
- *Field Emission Scanning Electron Microscopy (FE-SEM):* A Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operating at 5 kV was used to study the morphology of the opaque gel sample. The gel sample (20−30 mg) was dried under reduced pressure, coated (90 s, 2−3 nm thickness) with platinum, and then placed on a microscope cover glass.
- *Transmission Electron Microscopy (TEM):* A Philips CM-200 electron microscope working at an acceleration voltage of 200 kV was used to take the images of the opaque gel sample. The gel sample that is stained with 1% sodium phosphotungstate solution was deposited on the copper grid of 200 mesh size that was coated with the carbon Formvar.
- *Atomic Force Microscopy (AFM):* An atomic force microscope (Park XE 100) was used to investigate the morphology of the vacuum-dried (30 °C for 72 h) opaque gel sample by placing the dried gel sample on a microscopic glass.
- *FT-IR Spectroscopy:* The interaction involved in the phase transition from opaque to transparent was characterized through measuring the FT-IR spectrum of the partially dried gel samples (opaque and transparent) and solid C16EMorphBr sample on a Shimadzu FT-IR-8400S spectrophotometer. K)
- *Small-Angle Neutron Scattering (SANS):* SANS measurements for the gel samples were performed at sample temperatures of 25 and 50 °C on a Quokka (ANSTO, Australia). Data are presented as a function of the scattering vector, q, by using the incident neutron wavelength, λ, as where, a q range of 0.005−0.400 A°−1 was selected with 2 and 14 m as the sample-to-detector distances and 5 Å ($\Delta\lambda/\lambda$ =10%) as the incident wavelength. The experimental data were reduced from raw counts on the 2D detector to a radially averaged 1D scattering pattern with the assumption of radially isotropic scattering. The sensitivity of each detector pixel was calibrated by comparison of its response to a flat scatterer, and then the scattering from an empty SANS cell was subtracted. The scattering was then radially averaged (accounting for instrument configuration) to provide the intensity as a function of q. The absolute intensity scale was provided by normalizing each sample by its thickness (1 or 2 mm) and then comparing to either the scattering from an empty beam measurement. The data modeling program SAS view was used to fit the SANS data.
- *Tensile Strength Measurement:* Tensile tests of the xerogel were performed on a Testometric M100-1CT instrument with a loading rate of 75 mm min−1. The specimen had a thickness of 2.5 mm and width of 20 mm. The gauge distance between the clamps was 7 mm. Cyclic loading−unloading tests were performed by loading the xerogel under tension to strains of 200 and 500% and then unloading to zero force.

4.4 Multifunctional self-healing Eutectogels induced by supramolecular assembly for smart conductive materials, interface lubrication and dye adsorption:

It describes a self-healing eutectogel that has multifunctionality such as high ionic conductivity and self-healing property which makes it potentially useful in a smart ionic conductor. The eutectogel also has corrosion resistance and showed good lubricating performances on steel interfaces. In addition, the eutectogel showed excellent dye adsorption, effectively removing dyes from aqueous solutions[3] Deep eutectic solvents (DESs) are a special kind of ionic liquid formed by mixing a quaternary ammonium salt with a hydrogen-bond donor in a certain stoichiometric ratio, and the melting point is lower than that of the individual components. Like traditional ionic liquids, DESs have low volatility, good conductivity, low flammability, wide range of liquids, and electrochemical windows. They also have other advantages, including low cost, easy availability, and non-toxicity. These solvents are widely used in electrochemistry, material synthesis, separation and purification, and catalysis.[6]

X-DBS was synthesized by a condensation reaction between D-sorbitol and halogenated benzaldehyde. The gelation behavior was examined using the “stable to inversion of a test tube” method The gel-sol transition temperature was determined using a conventional ball-drop method. The xerogel was prepared by freeze-drying, followed by solvent exchange.[7]



X-DBS (X=F,Cl,Br)

ChCl

Urea

Gly

EG

MPG

PDO

Fig. 3 Chemical Structures of gelators X-DBS and DESs used.

Gelation ability of X-DBS: Five DES samples were prepared by mixing choline chloride (ChCl) and conventional hydrogen-bond donors (glycerol, ethylene glycol, monopropylene glycol, 1,3-propanediol, and urea) in a 1:2 M ratio. Then, the gelation performances of X-DBS were tested in the samples. The gelation behaviour, critical gel concentration (CGC) and gel-sol transition temperature (Tg) were determined to evaluate the gelation ability of the gelators in different DES samples. The storage modulus (G′) and recovery rate were determined to examine the mechanical properties and self-healing ability.(fig-9) At the same concentration, the G′ of the eutectogels formed by F-DBS in different DESs followed the order ChCl-urea > ChCl-Gly > ChCl-EG > ChCl-MPG > ChCl-PDO, and all the G′ values exceed 104 Pa, indicating good mechanical strength of the F-DBS-based Eutectogels.

Injectable and Self-Healing eutectogel:

Self-healing properties of the eutectogels, continuous step-strain scanning measurement was performed by alternately applying 0.1% and 25% strain at a fixed frequency of 1 Hz). The eutectogel quickly and completely recovered their mechanical properties after the first damage. The rate and degree of recovery remained almost constant after three cycles, indicating that the F-DBS-based eutectogel is reversible and durable. The self-healing property of the eutectogel could also be observed with naked eyes.Three samples of eutectogels were connected to form one integrated block within 0.5 h, Indicating the self-healing behavior. Notably, the F-DBS/ChCl-Gly eutectogel with a concentration of 2% could support a weight of 200 g, showing its load-bearing capacity Also, the viscosity of the F-DBS/ChCl- Gly eutectogel decreased gradually as the shear rate increased from 0 to 1000 s1, and its value gradually recovered to the initial state as the shear rate decreased, indicating the typical shear-thinning behavior and creep-recovery performance of the gel. These favorable properties endowed the eutectogel with injectability, thus, the F-DBS/ChCl- Gly eutectogel could be injected through a common syringe. The excellent properties of the eutectogels, including good mechanical strength, remarkable self-healing ability, and high electrical conductivity, make the eutectogels a promising multifunctional material with several applications. [3] Based on these results, we propose a feasible self-assembly mechanism for F-DBS in DES, as illustrated in (fig-11). DES can turn into supramolecular eutectogels by the addition of F-DBS (2% w/v), which self-assembles into nanofibers, forming supramolecular eutectogels. Upon mechanical damage, the hydrogen bonding interactions (between the C-F group and urea) located in the side chains of the fiber are weakened and broken in the damaged area, thereby reducing the strength of the gel. After removing the mechanical destructive force, the fibrous aggregates spontaneously diffuse and encounter again, reforming hydrogen bonds, and the eutectogel is repaired.[3]

Application of eutectiogel as an efficient material for dye adsorption:

Supramolecular gels have been proven to effectively remove various pollutants, such as dyes and oil spills from water[8], [9]. Moreover, as environmentally friendly and low-cost green solvents, DESs also show potential application performance in terms of dye adsorption. [10] Therefore, the FDBS-based eutectiogels are well suited to this “water purification” application as the filtration network of the gel matrix has a high surface area (as a consequence of its nanoscale structure, as verified by SEM and AFM) - which maximizes the potential interactions with pollutants.

4.5 Environmentally friendly eutectogels comprising L-Amino Acids and Deep Eutectic Solvents: Efficient Materials for Wastewater Treatment:

Eutectogels are a new class of materials that can be used for wastewater treatment. They are made up of deep eutectic solvents (DESs) and L-amino acids. DESs are a type of ionic liquid that is made up of two or more components that form a eutectic mixture. L-amino acids are the building blocks of proteins and are biodegradable. The combination of these two materials creates a gel-like substance that can be used to remove pollutants from wastewater. The article explains that eutectogels have several advantages over other materials used for wastewater treatment. They are environmentally friendly, biodegradable, and can be easily synthesized. They are also efficient at removing pollutants from wastewater.[11]

The development of non-conventional solvents, driven by sustainable chemistry, has impacted also the field of gels, giving rise to gels in ionic liquids known as ionic liquid gels (ILGs) and, very recently, in deep eutectic solvents (DES), yielding eutectogels.[11], [12]

General procedure for the preparation of DES:

The suitable amounts of phenylacetic acid and choline chloride were weighed in a round bottom flask. The resulting mixture was heated at 60 °C for 30 minutes and stirred until obtaining a limpid liquid, which was then dried under reduced pressure at 60 °C for 1 h and kept in a desiccator over calcium chloride.[11]

General procedure for the preparation of eutectogels:

Gels were prepared by weighing into a screw-capped sample vial (diameter 1 cm) the suitable amounts of amino acid and DES. The sample vial was heated in an oil bath at 80 °C for 30 minutes, during which a clear solution was obtained. The vial was then rapidly cooled at 4 °C and then left to stand at room temperature. The tube inversion test method was used to assess gel formation.[11]

Tgel determination:

Tgel were determined by the falling drop method. A vial containing the preformed gel was placed upside-down in a water bath. The bath temperature was raised gradually (1 °C/ min) until the gel collapsed and flow was observed. Tgel values were reproducible within 1 °C.[11]

Opacity Measurements:

Opacity measurements were recorded with a spectrophotometer. The opacity of the gel phases was determined with UV-Vis measurements as a function of time, at a wavelength of 568 nm at 25 °C. Samples for a typical measurement were prepared by injecting into a quartz cuvette (light path 0.2 cm) the limpid hot solution of salt, recording spectra until gel formation. The gel phase obtained at the end of the measurement was stable after the tube inversion test.[11]

Dye Adsorption tests:

Dye adsorption tests were firstly carried out in vials by placing onto the 250 mg of preformed eutectogel (3 wt %), 500 µL of a 1.8×10-4 M aqueous solution of dye. After a given time, an aliquot of solution was withdrawn, suitably diluted, then the relevant UV-vis spectrum was recorded. Concentrations were obtained based on calibration curves obtained by measuring the absorbance of aqueous solutions of the dye at increasing concentrations. The removal efficiency of gels was also investigated in a gel column using a previously reported procedure. To this aim, 1g of eutectogel were placed on the bottom of a column, (Æ=4 cm), whose septum was previously covered with a layer of sand. Blank experiments assured that no dye was adsorbed by the sand alone. Then, 3 mL of aqueous solution of the dye was added from the top of the column. An out flow of discolored water from the bottom of the column was observed and it was introduced again in a next column containing another aliquot of gel. This procedure was repeated a third time when clear water out flowing from the column was observed. The experiment was performed under atmospheric pressure and at 25 °C.

4.6 Conclusion:

A new type of materials for wastewater treatment, which are gels made from natural or synthetic polymers and green solvents. These gels have many advantages over conventional adsorbents, such as low cost, easy synthesis, biodegradability, and recyclability. They can also be modified to enhance their adsorption performance and selectivity for different contaminants. The abstract suggests that these gels are promising materials for the development of sustainable and efficient wastewater treatment technologies.

4.7 Reference:

1. C. Rizzo *et al.*, “Self-Sustaining Supramolecular Ionic Liquid Gels for Dye Adsorption,” *ACS Sustain Chem Eng*, vol. 6, no. 9, pp. 12453–12462, Sep. 2018, doi: 10.1021/acssuschemeng.8b03002.
2. M. Kuddushi *et al.*, “Stimuli Responsive, Self-Sustainable, and Self-Healable Functionalized Hydrogel with Dual Gelation, Load-Bearing, and Dye-Absorbing Properties,” *ACS Appl Mater Interfaces*, vol. 11, no. 21, pp. 19572–19583, May 2019, doi: 10.1021/acsami.9b01129.
3. K. Fan *et al.*, “Multifunctional self-healing eutectogels induced by supramolecular assembly for smart conductive materials, interface lubrication and dye adsorption,” *Chemical Engineering Journal*, vol. 441, p. 136026, Aug. 2022, doi: 10.1016/j.cej.2022.136026.
4. A. Baral, S. Basak, K. Basu, A. Dehsorkhi, I. W. Hamley, and A. Banerjee, “Time-dependent gel to gel transformation of a peptide based supramolecular gelator,” *Soft Matter*, vol. 11, no. 24, pp. 4944–4951, 2015, doi: 10.1039/C5SM00808E.
5. L. Han, Y. Zhang, X. Lu, K. Wang, Z. Wang, and H. Zhang, “Polydopamine Nanoparticles Modulating Stimuli-Responsive PNIPAM Hydrogels with Cell/Tissue Adhesiveness,” *ACS Appl Mater Interfaces*, vol. 8, no. 42, pp. 29088–29100, Oct. 2016, doi: 10.1021/acsami.6b11043.

6. J. Wu *et al.*, "Deep Eutectic Solvents for Boosting Electrochemical Energy Storage and Conversion: A Review and Perspective," *Adv Funct Mater*, vol. 31, no. 22, p. 2011102, May 2021, doi: 10.1002/adfm.202011102.
7. J. Ruiz-Olles, P. Slavik, N. K. Whitelaw, and D. K. Smith, "Self-Assembled Gels Formed in Deep Eutectic Solvents: Supramolecular Eutectogels with High Ionic Conductivity," *Angewandte Chemie International Edition*, vol. 58, no. 13, pp. 4173–4178, Mar. 2019, doi: 10.1002/anie.201810600.
8. A. P. Abbott, E. I. Ahmed, R. C. Harris, and K. S. Ryder, "Evaluating water miscible deep eutectic solvents (DESs) and ionic liquids as potential lubricants," *Green Chem.*, vol. 16, no. 9, pp. 4156–4161, 2014, doi: 10.1039/C4GC00952E.
9. L. Li *et al.*, "A supramolecular gel made from an azobenzene-based phenylalanine derivative: synthesis, self-assembly, and dye adsorption," *Colloids Surf A Physicochem Eng Asp*, vol. 628, p. 127289, Nov. 2021, doi: 10.1016/j.colsurfa.2021.127289.
10. sX. Guan, K. Fan, T. Gao, A. Ma, B. Zhang, and J. Song, "A novel multi-stimuli responsive gelator based on <scp>d</scp> -gluconic acetal and its potential applications," *Chemical Communications*, vol. 52, no. 5, pp. 962–965, 2016, doi: 10.1039/C5CC08615A.
11. S. Marullo, A. Meli, Nadka. Tz. Dintcheva, G. Infurna, C. Rizzo, and F. D'Anna, "Environmentally Friendly Eutectogels Comprising <scp>l-a</scp> mino Acids and Deep Eutectic Solvents: Efficient Materials for Wastewater Treatment," *Chempluschem*, vol. 85, no. 2, pp. 301–311, Feb. 2020, doi: 10.1002/cplu.202000017.
12. P. C. Marr and A. C. Marr, "Ionic liquid gel materials: applications in green and sustainable chemistry," *Green Chemistry*, vol. 18, no. 1, pp. 105–128, 2016, doi: 10.1039/C5GC02277K.